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Recent Development of Cellulose/ TiO_2 Composite in Water Treatment

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Abstract

Pesticides, hormones, pharmaceuticals, dyes, parasites, and heavy metals are common contaminants in aquatic environments; reaching the wastewater via domestic and industrial effluents affects human health. Heterogeneous photocatalysis techniques as an advanced oxidation process focus on removing these contaminants. On the other hand, recently, as the most abundant natural biopolymer globally, cellulose has attracted much attention. This review reviews recent research on the different applications of cellulose/TiO_2 in wastewater treatment, starting with a brief introduction to the background of wastewater and the different processes of wastewater treatment, especially advanced oxidation processes. Then, general information of titanium, the structure of titanium oxide (TiO_2), and TiO_2 mechanism in water treatment followed by cellulose structure and its modified forms. In the end, different applications of cellulose/TiO_2 in wastewater treatment are discussed. Also, the conclusion and future directions from my perspectives are given.

Keywords; Cellulose; TiO_2; Water Treatment; Photocatalysis.

1. Introduction

The world faces a water shortage, which is a great challenge, specifically in the Middle East. At the same time, due to the absence of water sources and/or water pollution, drinking water represent a major burden [1]. At the same time, the rapid increase in the world's population is increasing the demand for drinking water sevenfold. It expects that within the next 30 years, the population will increase up to 40%, increasing the requirement of water sources for agriculture, domestic, and industrial [2]. On the other hand, water pollution increased with the rapid Development of the global economy. This pollution hinders the further Development of the economy and affects people's health. According to United Nations, the water crisis would be the first global crisis in the 21st century. Accordingly, controlling water pollution is an urgent matter [3]. For example, metals are present in water from natural sources such as volcanoes, weathering, ore deposits, and anthropogenic activities such as industries, mining, agriculture, and wastewater irrigation [4]. The indication parameters of wastewater quality are total organic carbon, biological oxygen demand, chemical oxygen demand, and suspended solids. In industrial wastewater, these parameters are high and reduce the performance of conventional processes for the treatment of wastewater [5].

The common treatments for wastewater are ion exchange, adsorption, electrochemical, chemical deposition, and biotechnology. They include chemical, physical, and biological processes (**Fig. 1**). The selection of one of them depends on various factors such as sewage composition, dye concentration, additional impurities present in wastewater, and processing cost. Each method has distinctive features that can be beneficial but restricted in another. High running cost, low output, high processing time, and toxic by-products treatment methods are less considerable for applications. Subsequently, it is decisive to research an alternative method that completely removes or degrades contaminants. Recently, biodegradable, renewable, and sustainable materials for water treatment have been much attention [6-8]. Biopolymers are naturally occurring polymers with many features and properties such as renewable, non-toxicity, biocompatibility, biodegradability, bioactivity, low cost, and environmentally friendly than conventional polymers [9]. **Table 1** shows the advantage and disadvantages of different wastewater treatment techniques [10, 11].

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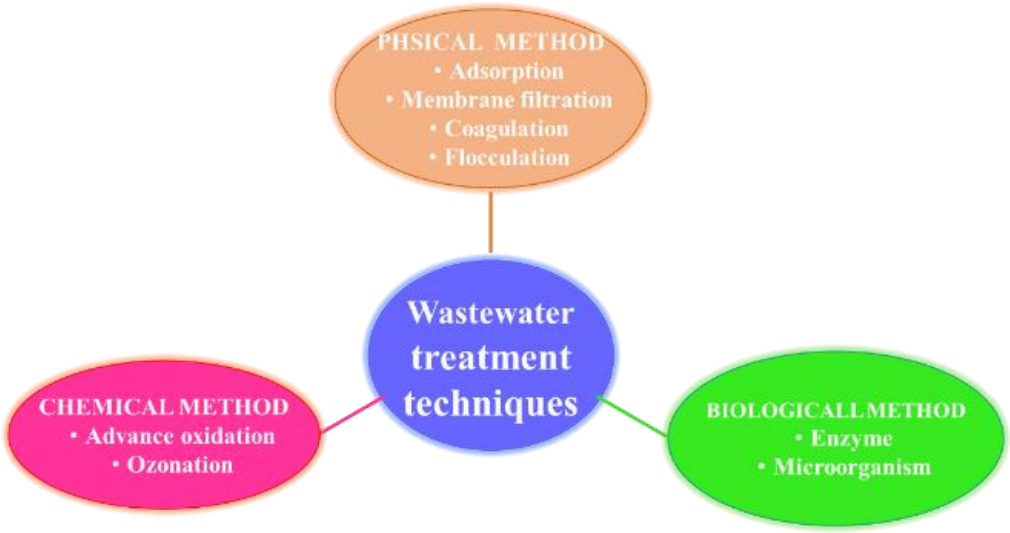

Fig. 1. Advanced and conventional techniques are used to treat wastewater [6].

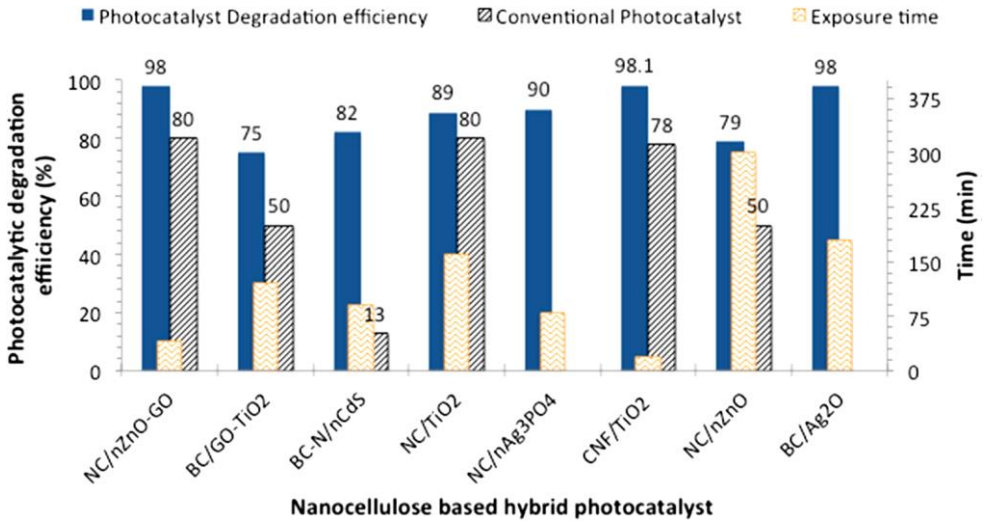

Fig. 2. The photocatalytic degradation efficiency of nanocellulose based nanohybrid photocatalysts [14].

Table 1: Advantages and disadvantages of wastewater treatment techniques.

Method	Advantage	Disadvantage
Chemical	• Simple. • Rapid. • Efficient processes. • Have multiple approaches.	• Laboratory scale techniques. • Economically not feasible for small industries to fulfill their energy requirements.
Physical	• Rapid and straightforward techniques. • Suitable for almost all types of pollutants like dyes, mineral ions, suspended particles, etc.	• Require high energy. • Not feasible for small industries as rapid membrane clogging occurs at high concentrations.
Physiochemical (Coagulation & flocculation)	• Simple physiochemical process.	• Cost challenging to handle sludge volume generation (large size flocs).
Biological treatment	• Simple. • Economically attractive technique.	• Slow process. • Low biodegradability. • Requires an optimally favourable environment and proper maintenance of microorganisms.

Researchers have combined nanocellulose with traditional metal oxide semiconductors to form a hybrid composite [12]. These hybrid composites offer more active sites due to increased surface area and wavelength response range in the visible light, improving metal ion adsorption to the catalyst's surface, thereby enhancing the effectiveness of photocatalytic degradation. Advantageously, photocatalytic membrane and film composites avoid the issues related to the recovery and removal of metal oxides suspension in water after photocatalytic organic degradation, as no residual photocatalyst is left behind in the reaction higher system [13].

The photocatalytic treatment is the advanced oxidation process to degrade organic contaminated in wastewater. Some metal oxides like TiO_2, Cu_2O, Fe_2O_3, ZnO, and CdS, and graphene oxide show photocatalytic action when exposed to UV and visible light irradiation [14]. **Fig. 2** shows the photocatalytic degradation efficiency of some metal oxide with nanocellulose as photocatalysts composites. During this treatment, the semiconductor absorbs photon energy that equals or exceeds the bandgap of the photocatalyst, the electron excited from the valence to the conduction band. It generates a hole in the valence band electron-hole (e^- - h^+) pair. This hole acts as an oxidizing agent and reacts with H_2O or OH^- giving hydroxyl radical. This hydroxyl radical rapidly reacts with organic compounds via e^--transfer, H^+ abstraction, radical addition, or radical combination, generating organic peroxide and C-centered radicals. These radicals react with organic contaminants and generate more active species such as H_2O_2 and superoxide ($^{o}O^{-}_{2}$), leading to chemical degradation. Also, the excited electron in the conduction band produces a hydroxyl radical, which combines with O_2 to form a superoxide radical that oxidizes the organic pollutant [15].

Despite the incompatibility interfacial between organic polymers and inorganic, the combination of inorganic and polymers is an attractive field in materials science [16]. Due to the superior characteristics of inorganic-organic hybrid materials, which combine the properties of inorganic and organic materials, these hybrid materials, especially inorganic nanoparticles/polymer composite materials, have attracted much attention [17]. The nano-size metals and metals oxides like TiO_2, ZnO, Au [18], Ag, CuO_2, and Fe_2O_3 have distinct size-dependent optoelectronic and physicochemical properties. Among these oxides, TiO_2 nanoparticles (TiO_2NPs) have attracted more attention due to their suitability for applications like solar energy conversion, photocatalysis for self-cleaning surfaces, photoelectronic activity, and water purification. Under UV or visible light irradiation, phenols, alcohols, carboxylic acids, and dye can be photodegraded by TiO_2NPs [19]. Also, the addition of TiO_2NPs onto cellulose improved the mechanical properties of the cellulosic membrane. For example, Nevstrueva et al. prepared TiO_2NPs blended cellulose membrane for the ultra-filtration process and investigated nanoparticle size's effect on membrane performance. They studied that TiO_2NPs with a size of 10 nm provides better antifouling properties than using a large particle size of 26-30 nm [20]. Gebru et al. fabricated ultrafiltration membranes from polyvinylpyrrolidone, TiO_2NPs, and cellulose acetate. The introduction of TiO_2NPs and polyvinylpyrrolidone into the polymer matrix improved the membranes' porosity, hydrophilic nature, and average pore size [21]. Moreover, a biocompatible scaffold was prepared from immobilization of 3-aminopropyltriethoxysilane into the cellulose with incorporated TiO_2NPs. This composite is a candidate for the regeneration of human skin fibroblast cells with a broad-spectrum antimicrobial activity [22].

2. Titanium

In 2019, about 62,000 tons of titanium scrap metal were consumed as follows; 50,000 by the titanium industry, 10,000 by the steel industry, 500 by the superalloy industry, and the remaining in other industries [23]. Titanium is the ninth most abundant element. Its average concentration is 4400 mg/kg in the earth's crust. In nature, it does not exist in the metallic state due to its affinity for oxygen. It excites in +2, +3, and +4 oxidation states; the naturally occurring oxide of Ti is Titanium dioxide (TiO_2), an odorless, incombustible, and white powder. Its molecular weight, boiling point, melting point, and relative density are 79.9 g/mol, 2972°C, 1843°C, and 4.26 g/cm^3, respectively [24]. TiO_2 has different crystal structures, and **Fig. 3** shows the crystal structures of TiO_2 polymorphs. Anatase, rutile, and brookite are most common, and anatase is more chemically reactive. Due to their widespread availability, anatase and rutile have been used and studied most [25]. The crystal structures of rutile and anatase belong to the tetragonal space groups $P4_2$/mnm, a = b = 4.593 Å, c = 2.959 Å, and $I4_1$/amd, a = b = 3.785 Å, c = 9.514 Å, respectively [26]. Anatase/rutile, 80/20, generated 6-fold more reactive oxygen species than rutile [27]. Anatase generates reactive oxygen species when UV light irradiates and does not generate under ambient light conditions [28]. TiO_2 nanoparticles (TiO_2NPs) are a mixture of anatase and rutile forms. The principal particles affecting their physicochemical properties include size, shape, inner structure, and surface characteristics [29]. It is possible to differentiate between anatase and rutile by various techniques. Raman spectroscopy is a useful technique for quickly characterizing anatase and rutile, and **Table 2** shows their different modes [30].

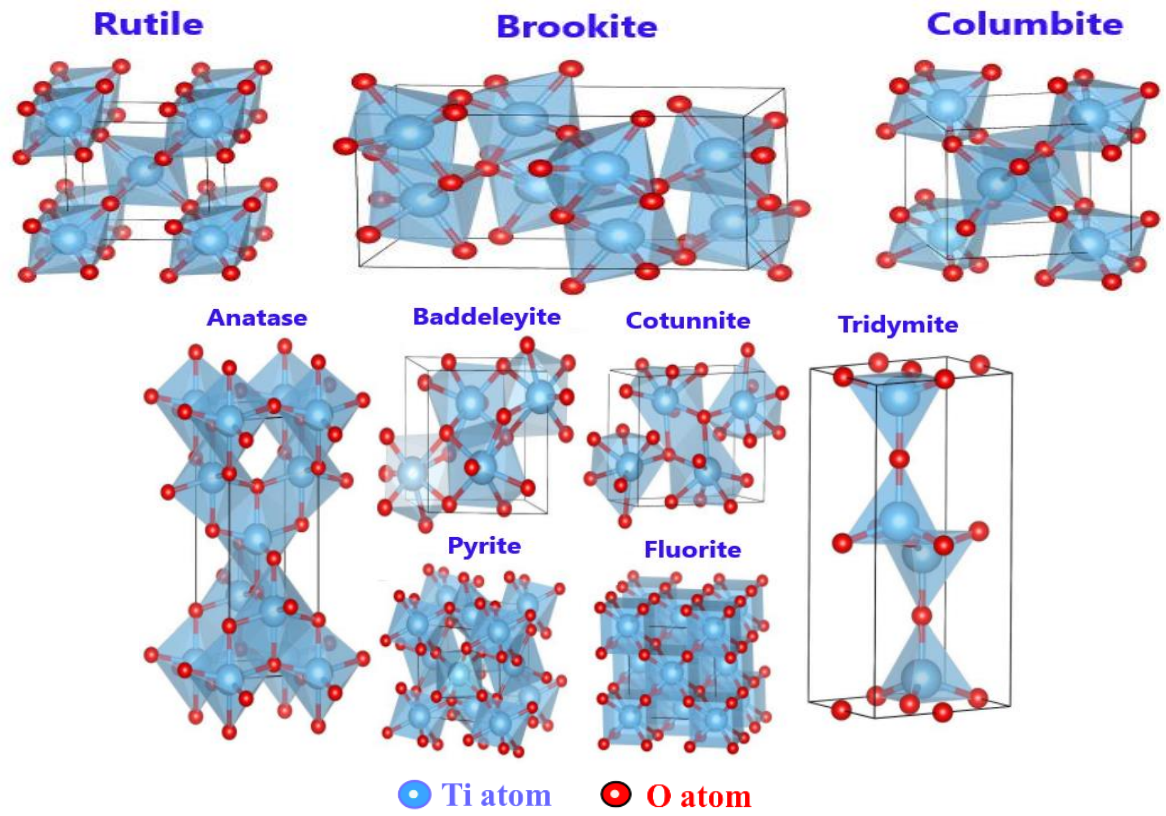

Fig. 3. Polyhedral structures for the TiO_2 polymorphs [31].

Table 2: Modes of anatase and rutile of Raman spectroscopy.

Mode	Raman shift (cm^{-1})	
	Anatase	Rutile
E_g	639, 197, 144	447
A_{1g}	513	612
B_{1g}	519, 399	143
B_{2g}	----	826

Another technique is the X-ray diffraction analysis which determines the sizes and phases of crystalline materials allowing the determination of the ratio of the anatase to the rutile phase. **Fig. 4** shows anatase and rutile X-ray diffraction patterns. The characteristic peaks of anatase are 2θ = 25.25° (101) and 2θ = 48.00° (101), while peaks at 2θ = 27.42° (110) and 2θ = 54.5° characterize the rutile phase. Anatase to rutile ratio can be estimated using the Spurr Meyers equation [32]:

$$XA\ (\%) = 100/((1 + 1.265\ IR//IA))$$

$$XR\ (\%) = 100/((1 + 0.8\ IA//IR))$$

Where XA and XR are the weight percentage of anatase and rutile IA is the anatase phase intensity at 2θ = 25.25°, IR is the intensity of rutile peak at 2θ = 27.42°.

TiO_2 is bio-inert and can be present in nanosized. It's nanosized manufactured worldwide in large quantities for use in various applications. It can be used as ingredients in paints, coatings, plastics, papers, inks, cosmetics like sunscreens and toothpaste, pharmaceutical, and food products [33-35]. In addition, TiO_2NPs can be used in the treatment of water contaminated [36], solar cells as a photoactive material [37], and catalytic reactions, like semiconductor photocatalysis.

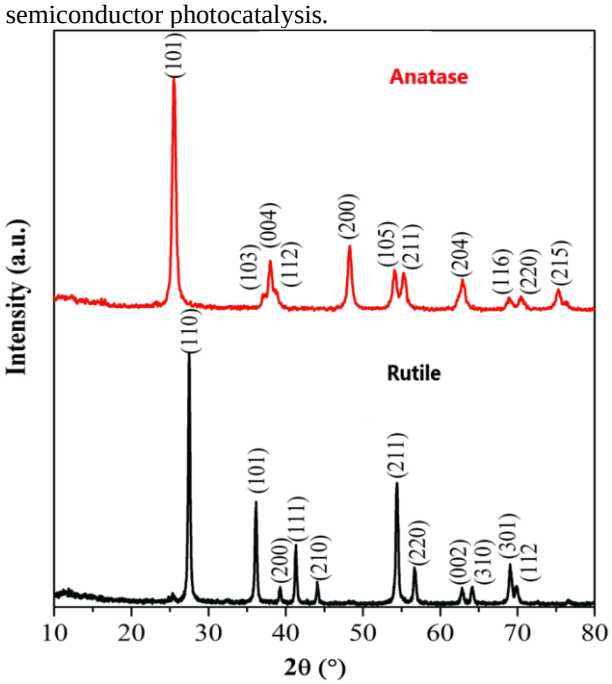

Fig. 4. X-ray diffraction patterns of anatase and rutile [30].

Also, it can be used for self-cleaning and anti-fogging purposes, such as self-cleaning textiles, self-cleaning windows, self-cleaning tiles, and anti-fogging car mirrors [38]. Therefore, human exposure may occur through ingestion, dermal penetration, or inhalation route during manufacturing and use. The main toxicity mechanism of TiO_2 involves the species' production of reactive oxygen, resulting in genotoxicity, inflammation, metabolic change, oxidative stress, and carcinogenesis. These effects depend on its physical and chemical characteristics, such as crystal structure, size, and photo-activation [39].

3. Cellulose

In 1839 Payen discovered cellulose as a linear homo-polysaccharide of β-D-glucopyranose linked by 1,4-glycosidic bonds [40]. Globally cellulose is the most abundant natural biopolymer, and it's chemically and thermally stable. Various processes isolate cellulose with varying fiber strengths of the pulp, e.g., bisulfite, alkaline, and sulfate processes, in combination with thermal and mechanical treatments [41]. The one end of the cellulose molecule chain is nonreducing (contains an anomeric C atom linked by the glycosidic bonds). In contrast, the other end is the reducing end group (which has a D-glucopyranose unit in equilibrium with the aldehyde function [42]. Natural cellulose can be transformed into nano- and microscale by applying specific top-down approaches, yielding microcrystalline cellulose, microfibrillar cellulose, and whiskers (**Fig. 5**). According to the using disintegration technique, these scales mainly differ in crystallinity and degree of polymerization and, consequently, differ in shape [43].

Compared to the diversity of applications of modified cellulose, pure cellulose has very few applications. Chemical modification of cellulose varies its properties such as absorptivity, microbial resistance, elasticity, hydrophilicity, hydrophobicity, mechanical, and heat resistance. The chemical modification starts at the primary hydroxyl at C6 followed by secondary hydroxyls at C2 and C3 [44]. The typical modifications of cellulose are etherifications and esterifications at the hydroxyl groups of cellulose. These substitution reactions prepare most water-soluble and organic solvent-soluble cellulose derivatives, and these chemical modifications can usually achieve drastic changes in the original properties of cellulose. Others are oxidation, acetylation, dehalogenation, and ionic and radical grafting [45, 46].

Cellulose is highly candidates as the host material of inorganic nanoparticles because it can control growth, improve stability, and retain the special morphology of nanoparticles. Also, cellulose can preserve excellent electrical, magnetic, and optical properties of inorganic nanoparticles. For example, conductive cellulose/polypyrrole-TiO_2 composites with/ without sodium silicate were prepared via in situ oxidative chemical polymerization of pyrrole using $FeCl_3$ as an oxidant [47, 48].

4. Applications in wastewater treatment

In the following sections, various strategies used in developing cellulose-loaded TiO_2 and its applications in the treatment of different populations of water will be discussed.

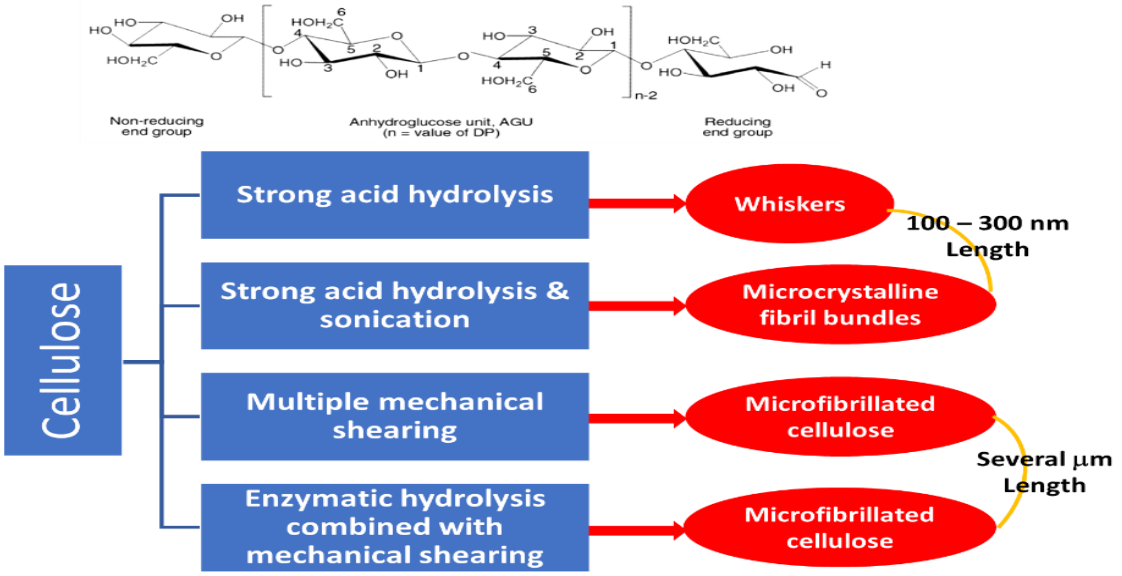

Fig. 5. Cellulose structure and different treatments for preparing nano- and microscale cellulosic materials.

4.1. Treatment of wastewater containing heavy metal ions

Examples of water contaminants heavy metal ions are cadmium, nickel, lead, chromium, cobalt, copper, and mercury. Due to their poisonousness, bioaccumulation capability, and persistency, thesis ions occur serious environmental pollution [49]. For example, excessive copper ions can cause anorexia, weakness, and lethargy [50]. Lead ion causes damage to the reproductive, blood circulation system, nervous, neurotoxicity, hematological, nephrotoxicity, and cardiovascular system [51]. Also, heavy metals are non-degradable and have a tendency to deposit in plants or living animals; they can cause numerous illnesses and sicknesses [52]. As the adsorption method is one of the most common processes to eliminate heavy metals ions from wastewater, the adsorption capacities, adsorption capacities, and specific surface area must be taken into consideration during the adsorption process. [53]. Polymer/inorganic oxides is the most proper material for the adsorption process [54]. Among the TiO_2 composite adsorbents, the efficiency of the adsorbent to cation exchanges depends greatly on the pH values of the intermediate. As at pH > 7, the OH groups on the TiO_2 surface make the adsorbent surface more negatively charged. Accordingly, the positively charged metal ions interact with the adsorbent surface and continue since the competition among H^+ and heavy metal ions is reduced [55]. At alkaline solution (high pH), the metal cations react with hydroxide ions to form metal hydroxide and precipitate [56]. The possible mechanism for eliminating Pb (II) ions by TiO_2 is monodentate inner-sphere-type surface complexation, according to Kim et al [57]. While Gebru et al. suggested the mechanisms for copper and lead eliminating as [58]:

$Ti{-}OH + Pb^{2+} \leftrightarrow Ti{-}O{-}Pb^{+} + H^{+}$

$Ti{-}OH + Cu^{2+} \leftrightarrow Ti{-}O{-}Cu^{+} + H^{+}$

Electrospun cellulose acetate/ TiO_2 adsorbents were prepared using the electrospinning technique by Gebru et al. They found that the highest removal efficiencies of lead and copper ions were 99.7% and 98.9% under the optimized conditions. In addition, the repeated adsorption-desorption after four phases showed high elimination capacity [58].

Anion exchanger from Fe(III)-coordinated amino-functionalized poly(glycidyl methacrylate)-grafted TiO_2-densified cellulose was prepared for the adsorption of As(V) from aqueous solutions. This exchanger could be used for four operations cycles without any appreciable decrease in adsorption capacity [59].

TiO_2 nanocrystals were immobilized on the surface of cellulose fibers via hydrolysis of $TiOSO_4$, giving TiO_2/cellulose nanocomposite. In this case, cellulose was acted as a scaffold to immobilize TiO_2, and as a chemical template-directed, the crystal growth formed spindle rutile of TiO_2 nanocrystals without agglomeration. The nanocomposite had high adsorption capacity, good renewability, and selectivity for Pb^{2+} removal. The capacity of the composite is 4 times higher than pure cellulose fiber. The adsorption capacity of the composite was 371.0 mg/g compared with 20.0 mg/g of commercial TiO_2 alone and higher 12-folds compared to the pure cellulose fiber bed [60].

4.2. Treatment of wastewater containing pigments and dyes

Pigments and synthetic dyes are widely used in textiles, pharmaceutical, and tannery industries that generate colored wastewater [61]. For example, 10 – 50 % of dye losses in the textile industry and discharged in the effluent during the dying process [62]. Due to a large amount of discharge and the degradation-resistant composition, textile wastewater is considered a major source of pollutants from the industry. The textile industry has several stages: sizing fibers, scouring, de-sizing, bleaching, rinsing, mercerizing, dyeing, and finishing (**Fig. 6**) [63]. As seen in **Fig. 6**, large quantities of organics are involved during the textile process. In addition, due to the production of various textiles nowadays, many contaminants are released into the environment through indiscriminate discharge of wastewater. According to some reports, textile wastewater contains dyes, grease, oil, detergents, fibers, heavy metal, and inorganic salts. However, dye residue is considered a dominant pollutant mainly produced in finishing [64]. Dyes in the water environment reduce light penetration and inhibit aquatic organisms' growth by reducing dissolved oxygen [65]. So, there is a need to remove dyes from industrial wastewater before entering the environment. Generally, the dyes have a complex aromatic structure that makes them unmanageable. Due to their refractory nature cannot be completely removed by conventional biological treatment or require a longer time for complete degradation. The advanced oxidation processes generate hydroxyl radicals ($OH^{\bullet}$) to oxidize the contaminants of the wastewater [66].

The heterogeneous photocatalytic oxidation process focuses on treating recalcitrant compounds in industrial wastewater. Due to high photocatalytic activity, non-toxicity, chemical stability, and the economically viable of TiO_2NPs, it has been widely used as a photocatalyst for dye degradation. TiO_2NPs have a high degree of bandgap energy (3.2 eV) and anatase absorption only in the UV region [67]. Solar energy consists of 46 and 6 % of visible and UV regions. Accordingly, the application of TiO_2 with external UV irradiation was extensively used for the treatment of industrial wastewater [68]. According to a previous report, some organic dyes are capable of photosensitizing TiO_2 due to the absorption of visible light [69], and the following equations show the photosensitization reactions [70]:

$$dye + h\nu \rightarrow dye^{*}$$

$$dye^{*} + TiO_2 \rightarrow dye^{\cdot +} + TiO_2 (e)$$
$$TiO_2(e) + O_2 \rightarrow TiO_2 + O^{2\cdot -}$$
$$O^{2\cdot -} + TiO_2(e) + 2H^+ \rightarrow H_2O_2 + TiO_2$$
$$2O^{2\cdot -} + 2H^+ \rightarrow O_2 + H_2O_2$$
$$H_2O_2 + TiO_2(e) \rightarrow {}^{\cdot}OH + OH^- + TiO_2$$
$$dye^{\cdot +} + (O^{2\cdot -} \text{ or } {}^{\cdot}OH) \text{ the degraded products}$$

TiO_2, anatase phase and rod-like structure, was successfully doped in microcellulose by Rajagopal et al. to decolorize methylene blue dye in sunlight. Hydrogen peroxide was added to assist the photocatalytic degradation. The optimized hydrogen peroxide/TiO_2/ microcellulose composite was removed 99% of methylene blue, acid violet, and methyl violet in the presence of sunlight during the decolorization of the wastewater process. And this composite was successively reused in four trials for dye degradation [71]. Also, spherical bacterial cellulose/TiO_2 nanocomposite was prepared by ex-situ and in-situ methods for contaminants removal from wastewater by photocatalysis process. The removal of methylene blue was 70.83 and 89.58 % by bacterial cellulose/TiO_2 nanocomposite in-situ and ex-situ, respectively [72]. In comparison, a polyaniline/carboxymethyl cellulose/TiO_2 nanocomposite was synthesized and used to absorb congo red from an aqueous solution. It was found that the optimal adsorption conditions at pH of 2.6, initial concentration of 82 mg/L, the temperature of 56 °C, adsorption time of 24 min, and adsorbent dose of 0.14 g. The adsorbent was also reusable without significantly changing adsorption capacity for at least five adsorption-desorption cycles [73].

HNO_3 or H_3PO_4 acids treated microcrystalline cellulose, impregnating Ti-alkoxide, giving photocatalysis adsorbents for photodegradation of orange-G dye in aqueous solutions under UV irradiation [74]. The cellulose acetate/TiO2 ultrafine fibers with different amounts of TiO2 NPs were prepared by the electrospinning process for dyeing water treatment. Photocatalytic degradation of the dye showed that with 5 wt% TiO_2, the degradation was as high as 90% after 240 min degradation and was effective for cycling use in dyeing water treatment [75].

To increase the photoactivity of TiO_2, a three-layer structured photocatalytic cellulose/ Au-TiO_2 membrane was fabricated through the tape casting method and the suction filtration process for the degradation of dye wastewater and use of solar energy for clean water regeneration. The addition of AuNPs on the surface of cellulose could eliminate the electron/holes recombination and increase the light absorption in the visible range due to the plasmon of Au [76]. The mechanism of photocatalytic water treatment explained according to Huang et al. as follows; Ti (IV) + $e^- \rightarrow$Ti (III); Ti (III) + $O_2 \rightarrow$Ti (IV) + $O_2^{\bullet -}$; $O_2 + e^-$ (Au)$\rightarrow O_2^{\bullet -}$; $H_2O + h^+ \rightarrow OH^{\bullet} + H^+$; $OH^{\bullet}$ + R → intermediates → $H_2O + CO_2$; $O_2^{\bullet -}$ + R → intermediates → $H_2O + CO_2$, where R represented contaminants. The reactive oxidizing substances such as O_3, $O_2^{\bullet -}$, O_2, $^{\bullet}OH$, and H_2O_2 could be produced on the surface of TiO_2 in the liquid and gas phases and doping of Au ion onto TiO2 leading to TiO_2 have a lower energy level than that of TiO_2 alone. These reactive species could react with contaminants to produce small non-toxic molecules [77].

4.3. Treatment of wastewater containing organic

Phenol is a volatile and low soluble in water organic material used in inks, detergents, and paints. Hence, most phenols escape into the air, harming the environment and the human body [78]. The synergy between cellulose and TiO_2 can improve the decomposition of the phenol under light irradiation. A photocatalytic film was prepared from regenerated cellulose from waste newspapers and N-doped anatase/rutile mixed-phase TiO_2 nanorods via phase transformation technique using aqueous NaOH/ urea solution. This film could degrade phenol and methylene blue in water solution under ultraviolet and visible light irradiation with degradation percentages of 96% and 78.8%, respectively [79, 80]. Cellulose/TiO_2 membrane consisted of nitrogen dopant incorporated in the TiO_2 lattice structure. This dopant N introduced localized N 2p states above the valence band improved the absorption capability under visible light irradiation [81]. Also, the N doping converted Ti from 4 to 3-state by charging compensation. In TiO_2, the 3d orbital of the 3-state formed donor energy below the conduction band, which also contributed to the visible light absorption in N-doped TiO_2 [82]. Consequently, N-doped TiO_2 nanorods within the cellulose matrix promoted photoactivation in visible light and UV irradiation (**Fig. 7**).

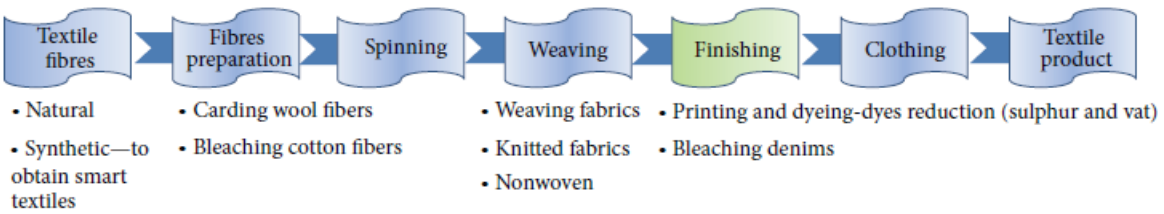

Fig. 6. Textile processes [64].

In another study, regenerated cellulose/TiO_2/ZnO nanocomposites have been prepared via hydrothermally grown ZnO on the regenerated cellulose/TiO_2 nanofibers by electrospinning technology followed via sol-gel process. The regenerated cellulose/TiO_2/ZnO nanocomposites perform a higher photocatalytic degradation of organic compounds than regenerated cellulose/TiO2 nanocomposites nanofibers or pure ZnO nanosheets [83]. Also, TiO_2/cellulose composite films with good photocatalytic activity in phenol degradation under weak UV light by in situ syntheses TiO_2NPs in the regenerated cellulose matrix via a sol-gel method. Cellulose was dissolved in the urea/NaOH system and regenerated by Na_2SO_4 solution. Also, these films had high mechanical properties, leading to the reusable portable catalyst in the photodegradation of organic pollutants [84]. A hybrid hydroxypropyl methylcellulose/TiO_2 composite was prepared with different weight ratios by a simple in situ method for the degradation of nitrophenol. It was found that the in-situ hybridization significantly increased TiO_2 specific surface area and extended its light absorption range to the visible region. Consequently, this composite was photo catalytically more active than pure TiO_2. The composite with 5% TiO_2 achieved the best performance due to the enhancement of surface coverage of nitrophenol on the photocatalyst, accelerating the migration rate of nitrophenol toward the surface of the photocatalyst expanding the wavelength response range. Also, the composite could be reused five times with the only gradual loss of activity [85].

On the other hand, Mefenamic acid (dimethylphenylamino benzoic acid) is widely used as an effective anti-inflammatory, antipyretic, and analgesic agent. It decomposes into toxic metabolites by being released in the aquatic environment [86]. Nanocellulose -supported TiO_2NPs for the photodegradation of mefenamic and anthranilic acids as derivatives drugs were prepared using ultrasonic impregnation. The TiO_2 content played an important role in the adsorption/photodegradation process. The highest sorption potential was shown with 10 wt% TiO_2 (22.43 mg/ g) and more than 85% photocatalytic activity even after five cycles [87]. In addition, the use of pesticides during the growth cycle of plants causes an environmental problem in the accumulation of its intermediates into soils. Consequently, these intermediates chemicals are transmitted via crops to users and accumulate in both [88]. Photocatalyst was fabricated by embedding TiO_2NPs into carboxymethyl cellulose/Tryptophan hybrid material using microwave assistance and used as a catalyst for photodegradation of 2,4-dichlorophenol (pesticide intermediate). It was found that the rate of degradation was increased by 11.6 times with 4% TiO_2 [12].

4.4. Treatment of bacteria lived wastewater

Bacterial infection through water pollution is one of the big challenges that seriously endanger human health. It is necessary to develop new antibacterial materials to prevent this infection, and antibacterial nanomaterials like TiO_2 are newly developed materials [89]. The antibacterial mechanism is that under UV-light irradiation, TiO_2 absorbs photons and reacts with water and oxygen, leading to the formation of reactive oxygen species [90]. Overproduction of reactive oxygen species induces oxidative stress, resulting in cells failing to maintain normal physiological redox-regulated functions [91]. The TiO_2 enwrapped GO as hybrid nanoparticles were prepared by a sol-gel method and impregnated into bacterial cellulose. The calcined temperature played a major role in photocatalytic activity. The antibacterial activity under the near-UV irradiation of the prepared composite was dose and irradiation time-dependent. An antibacterial rate of 91.3% accompanied the maximum photocatalytic activity [92].

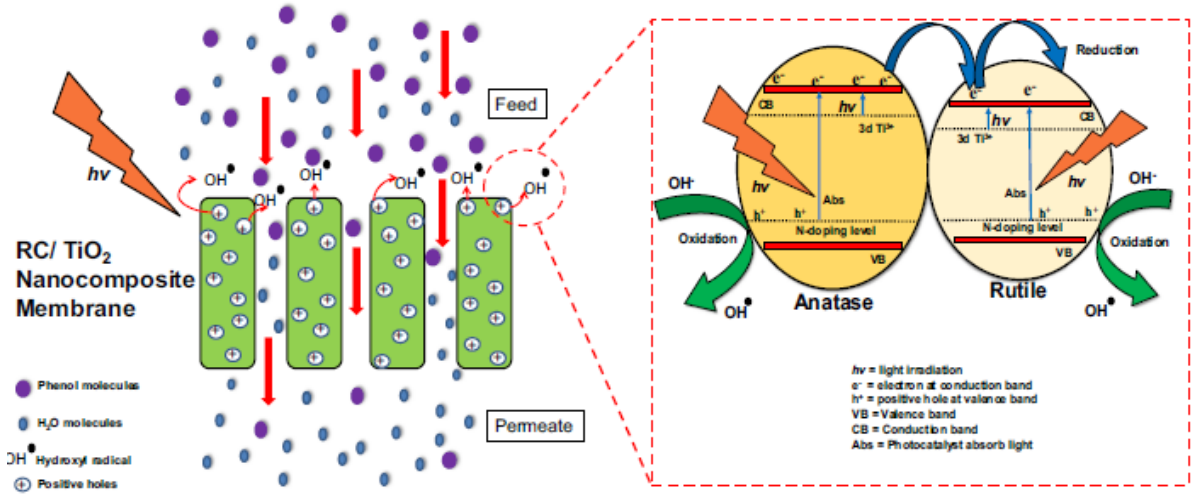

Fig. 7. The degradation process of phenol with regenerated cellulose membrane (*left*). Photocatalytic mechanism over the N-TiO_2 anatase/rutile mixed-phase (*right*) [79].

5. Conclusion and future directions

- Developing an efficient, low-cost, and green method for wastewater treatment is essential for protecting the environment.
- The biological effects are still not completely elucidated; thus, a deep understanding of the toxicological profile of TiO_2 is required.
- Although, during the past decades, researchers focused on photocatalysis as an effective process for wastewater treatment, the industrial application is still in an infantile stage.
- The efficiency of solar utilization, the construction, and the operation of photoreactors are still challenges.
- The design of photoreactors is also needed to optimize the operational factors for the system's activity.
- Finally, cellulose-loaded TiO_2 in the photocatalysis method is a promising pathway for treating pollutants in wastewaters.

Declaration of competing interest

The author declares that he does not have any conflict of interest.

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